Effect of Electric Fields on the Far Infrared Absorption
Cross-section of Liquid Aniline

BY GARETH J. EVANS AND MYRON W. EVANS*
Chemistry Department, University College of Wales, Aberystwyth SY23 1NE

Received 24th September, 1979

Some electric field induced intensity changes in the far infrared spectrum of liquid anilines are interpreted qualitatively in terms of the dynamical internal field theory of Lobo et al., based on the concept of dielectric friction. Several of the relevant models of molecular motion are inter-related for ease of interpretation.

Far infrared absorption spectra of nitroanilines have been used recently by Ascarelli et al. to discuss collective modes in liquids with sufficiently high dipole moments and therefore pronounced intermolecular interaction. The mathematical foundation for the existence of these collective modes (transverse and longitudinal) comes from a theory by Lobo et al., based on the treatment of internal (or re- laxation) field due to Nee and Zwanig. Here the relaxation field does not follow the motion of the dipole instantaneously but in a "retarded" fashion, due to what is termed dielectric friction.

The existence of electric field induced infrared intensity changes has emerged from the analysis of Lippert and Michel of pure liquid acetonitrile. Some bands are sensitive to the application of external electric fields, their absorption intensity cross-section being considerably depleted. This effect is opposite to that of temperature.

The purpose of this paper is two-fold: (1) to present some far infrared spectra of aniline as a function of applied electric field; (2) to coordinate the theories of the far infrared available in the literature in preparation for a more detailed analysis of the experimental data.

The paper is developed as follows. Firstly we interrelate the theories. It emerges that the equations used by Lobo et al. are those of Evans et al., or alternatively of Kivelson and Madden for the dynamical internal field using the concept of dielectric friction, introduced by Saufl, Patuzzo and Mason and Nee and Zwanig. The work of Kivelson and Madden allows us to relate the single particle auto-correlation function ($C_{Q}(t)$ = $\langle u(t) \cdot u(0) \rangle$), where $u(t)$ is the dipole vector) to the full (multi-particle) cross-correlation function $C_{Q}(t)$ observable experimentally. Although Lobo et al. speak of collective modes, both transverse and longitudinal, their theory is concerned only with $C_{Q}(t)$, i.e., with the autocorrelation function. The mosto-micro theorem of Kivelson and Madden states that $C_{Q}(t)$ has the same mathematical dependence on $t$ as $C_{Q}(t)$, although the constants of the equation are different.

Secondly, the experimental arrangement and results are described and lastly the results are discussed in terms of collective response to the applied electric field.
The expression devised for \( C_w(t) \) by Nee and Zwanizig \(^a\) may be written as:

\[
\mathcal{P}[-C_w(t)] = \left[ 1 - \frac{n^2}{d(0)} \frac{\phi(w)-\phi(0)}{2\pi^2 (w^2+n^2)} \right]^{-1}
\]

(1)

where \( \tau_0 \) is the microscopic relaxation time, inversely proportional to the rotational diffusion constant (or friction coefficient), \( n \) is the refractive index at the end of the far infrared dispersion (which is not \( n_a \)) and \( \phi(w) \) is the complex permittivity. \( \mathcal{P} \) is the Laplace-transform operator. The relaxation time \( \tau_0 \) is due to the van der Waals and not the long-range dipole-dipole and other types of electrodynamic interactions. When there is no internal field correction, or when \([\phi(0)-n^2] \) is small, we have:

\[
\mathcal{P}[-C_w(t)] = (1-\frac{n^2}{d(0)})^{-1}
\]

(2)

the Debye equation. Eqn (1) may be rewritten as:

\[
\mathcal{P}[-C_w(t)] = (1-\frac{n^2}{d(0)})^{-1}
\]

(3)

where \( \tau(\omega) = \frac{\tau_0}{(2\pi \omega)} \) and is memoryless in the sense that \( \tau_0 \) defined by:

\[
\tau(\omega) = \frac{\tau_0}{(2\pi \omega)}
\]

is independent of frequency. Here \( \tau_0(\omega) \) is the dielectric friction term and \( \tau_0 \) the hydrodynamic.

In deriving eqn (1) the assumptions are made that: (i) The Euler equations are linearized in the angular velocity \( \omega \). In general all three components of \( \omega \) are coupled. (ii) The Liouville equation for the conditional probability density function \( f(w(t), \omega(0), \tau_0) \) is solved in a Gaussian approximation.

Now we may introduce inertial and memory effects by one of two means. Firstly, following Lobo et al. we may write the Langevin equation for the Cartesian components of the angular velocity \( \omega \), i.e., for each component:

\[
\dot{\omega} = -\int_0^\tau dt \mathcal{K}_c(t-\tau)\omega(t) + N_\omega(t).
\]

(4)

Here \( N_\omega(t) \) is a random torque due to van der Waals interactions (short-range).

If the torque autocorrelation function is assumed to be exponentially decaying then for each component:

\[
\langle N_\omega(t)N_\omega(0) \rangle = \langle N(t) \rangle \exp(-\tau/t)
\]

(5)

then it follows that eqn (1) is modified to:

\[
\mathcal{P}[-C_w(t)] = 1 - \frac{n^2}{d(0)} \frac{\phi(w)-\phi(0)}{2\pi^2 (w^2+n^2)}
\]

\[
- \int_0^\tau t \mathcal{K}_c(t-\tau) \frac{\langle N_\omega(t)N_\omega(0) \rangle}{2\pi^2 (w^2+n^2)}
\]

(6)

The rotational dynamics of an asymmetric top are complicated but the exact asymptotic expansion of \( \phi(w) \) depends only on a weighted average of the inverse of the inertial tensor. This is:

\[
\frac{1}{I} = \frac{1}{I_1} + \frac{1}{I_2}
\]

(7)
where \( I_2 \) and \( I_4 \) are the principal moments of inertia about axes normal to the dipole moment. Eqn (7) is that for \( I^* \), the effective moment of inertia to be used in a spherical equivalent of an asymmetric top. Secondly, we note that the r.h.s. of eqn (6) may be written as \( p = \langle p = 0 \rangle + (2kT/\hbar)(\langle N^2 \rangle/2kT)^2 \) where \( \langle N^2 \rangle \) are the rotational electric field corrections neglected. This term is exactly the form used by Evans et al. to describe the zero-THz absorption of gases, liquids, and gas-phase molecules. In the notations of these papers:

\[ \gamma = \tau/ \tau_{0}; \quad K_0 = 2kT/\hbar^2; \quad \beta_0 = \langle N^2 \rangle/I^*kT. \]

The term (8) is therefore also subject to the geometrical constraints of linearisation in the Euler angles, i.e., the diffusing asymptotic top is treated as a spherical top. The effect of this approximation is small when memory effects are neglected, but in the nematic phase the molecules are not spherically, this mathematical convenience might give rise to non-spherically. The question of extending the Zwanzig/Lobo formalism to the nematic phase is under consideration.

The complete expression derived by Lobo et al. for the complex permittivity \( \epsilon^*(\omega) = \epsilon(\omega) + i\gamma(\omega) \) is therefore equivalent to the expression (8) corrected for dielectric friction, as envisaged by Nees and Zwanzig. With this correction the permittivity is governed by:

\[
\left[ \epsilon^*(\omega) - \epsilon^* \right] = \frac{\epsilon^* \omega^2}{2kT} \left[ 1 + \frac{\gamma}{\tau_0} \right] \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right] \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right]^* = \frac{\gamma \epsilon(\omega) - \epsilon^* \gamma \omega^2}{2kT} \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right] \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right]^* \]

\[ \epsilon^*(\omega) = \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \]

\[ z^2 = 1 + \frac{n^2}{\tau_0} \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right] \]

where \( \tau_0 = \langle N^2 \rangle/\gamma/2kT \) or, solving for \( \epsilon^*(\omega) \), after Lobo et al.,

\[
\epsilon^*(\omega) = \frac{1}{2} \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right] \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right]^* \]

\[ z^2 = \frac{1 + \frac{n^2}{\tau_0}}{\epsilon(\omega) + i\gamma} \]

where \( \epsilon^* = \epsilon_0/\tau_0 \). The effect of dielectric friction on the far infrared spectrum of eqn(8) is illustrated in fig. 1 for various values of \( \epsilon(\omega) \) and \( \gamma \).

We remark to close this section that the equivalent of eqn (8) has been derived by Kivelson and Madden; their three variable macro-micro correlation theorem linking the single particle autocorrelation theorem \( C_{\omega}(\omega) \) to the multiparticle cross-correlation function \( C_{\omega}(\omega) \). In their notation:

\[
C_{\omega}(\omega) = \frac{1}{\tau_0} \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right] \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right]^* \frac{1}{1 - 2\alpha_0 \alpha^*} \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right] \left[ \frac{\epsilon(\omega) + i\gamma}{2 \epsilon(\omega) + i\gamma} \right]^* \frac{1}{1 - 2\alpha_0 \alpha^*} \frac{1}{1 - 2\alpha_0 \alpha^*}.
\]
This expression is identical with the three variable theory of Questecree and Bzor, developed by Evans et al. We have

\[ \tau = r^{-1} = \tau_{ST}; \]

\[ \frac{\langle N_2^2 \rangle}{2(kT)^2} = \frac{K_4(D)}{K_4(E)} \left[ \left( \frac{d^2 \cos \theta / dt^2}{} \right)^2 - 1 \right] \]

Here \( \tau_{ST} \) is a single-particle correlation time associated with intermolecular torques. It is related to a single particle orientational correlation time \( \tau_{OP} \) by:

\[ \tau_{OP} = \left[ \left( \frac{d^2 \cos \theta / dt^2}{} \right)^2 - 1 \right] \frac{1}{3kT}. \]
Fig. 1. (a) Effect of dielectric friction on the far infrared power absorption coefficient $\alpha \langle \omega \rangle$ and dielectric loss $\varepsilon' \langle \omega \rangle K_0(\omega)$: $K_0(\omega) = 2 \times 10^{10} e^{-\omega^2}$; $K_0(\omega) = 17 \times 10^{10} e^{-\omega^2}$; $\gamma = 6 \times 10^{10} e^{-\omega^2}$; $\alpha_0 = 4.0$; $\alpha^2 = 2.0$. (1) Evans et al., three variable theory (no external field); (2) Labo et al. Sou (196); $-$, $\varepsilon' \langle \omega \rangle$; $-$, $\varepsilon'' \langle \omega \rangle$. The intensity decrease due to the internal field, interpreted in terms of dielectric friction, increases in fig. 3, induced by an external electric field. (b) $\alpha_0 = 2.0$; $\alpha^2 = 5.0$, $K_0(\omega) = 1.4 \times 10^{10} e^{-\omega^2}$; $K_0(\omega) = 15 \times 10^{10} e^{-\omega^2}$; $\gamma = 6 \times 10^{10} e^{-\omega^2}$. The greater the diffusivity $\varepsilon'' \langle \omega \rangle$, the greater is the relative decrease in absorption cross-section. (c) $\alpha_0 = 2.0$; $\alpha^2 = 3.0$, $K_0(\omega) = 2.69 \times 10^{10} e^{-\omega^2}$; $K_0(\omega) = 7.22 \times 10^{10} e^{-\omega^2}$; $\gamma = 6.8 \times 10^{10} e^{-\omega^2}$. (d) $\alpha_0 = 2.0$; $\alpha^2 = 3.0$, $K_0(\omega) = 1.52 \times 10^{10} e^{-\omega^2}$; $K_0(\omega) = 2.0 \times 10^{10} e^{-\omega^2}$; $\gamma = 2.4 \times 10^{10} e^{-\omega^2}$.
The use of the three variable models with a Fattazza/Mason type of internal field correction is equivalent to the theory of Lobo et al. These models are known \( n \) to \( \alpha_2 \) to break down under certain limits; the experimental case of highly viscous or glassy media is one of these and another is the approach to free rotation. However, the predicted frequencies of the longitudinal \( \alpha_0 \) and transverse \( \alpha_2 \) "collective" modes are:

\[
\alpha_0^2 = \alpha_1^2 + \alpha_2^2
\]

where

\[
\alpha_0^2 = 4n(N/V)(\bar{d}/4d_0^2)(n^2 - 2)^2/\rho e^2
\]

and

\[
\alpha_2^2 = (kT/P)(1 - 2\alpha_0^2/\lambda)
\]

Ascarello has made use of the fact that the longitudinal mode does not couple to a transverse electromagnetic wave incident normal to the surface, in order to identify \( \alpha_0 \) and \( \alpha_2 \) experimentally. The longitudinal wave can be picked up when the electromagnetic wave has an oblique angle of incidence on the surface of the liquid specimen. The values for \( \alpha_0 \) and \( \alpha_2 \) are in agreement with those calculated from the theory of Lobo et al. Ascarello also discovered by means of reflectivity a significant effect of an external electric field on the "collective" electrodynamical modes. The effect of an externally applied electric field favours the growth of clusters or aggregation of dipoles in the liquid so that the local dipole density may differ very much from its average value. The resulting value of \( \alpha_0 \) then has a distribution which depends on the local dipole density. Even in as dilute a solution as 10 % nitromethane in carbon tetrachloride observed \( \alpha_2 \) shifts from \( 3 \times 10^3 \) to \( 6 \times 10^3 \) cm\(^{-1}\). In the sections below we present some electric field affected far infrared spectra of the hydrogen-bonded system, aniline, and qualitatively assess their significance in the light of these remarks.

**EXPERIMENTAL**

The standard interferometric technique of far infrared power absorption spectroscopy was used with an NPL/Graph-Pariate "cube" spectrometer. The electric field cell was constructed from a "(meth-acryl-pen-1-ene)" and was designed for field application perpendicular to measuring electromagnetic radiation. Electric fields (both static and alternating) were applied. Alternating fields of up to 3 kV at 1 kHz were used and static fields of up to 6 kV across an electrode gap of 25 mm in a cell otherwise constructed similarly to "(pol-y methyl-pen-1-ene)". Conductivity measurements were made on all the samples employed. There does not appear to be a correlation between this quantity and the electric field effects. The response of the integrated absorption intensity to the field application is illustrated in fig. 2. This could be roughly measured to less than a second with the means at our disposal.

**RESULTS**

When a static or alternating electric field is applied perpendicular to the measuring, electromagnetic beam the far infrared absorption (fig. 3) decreases, as observed for a liquid CH\(_2\)CN near infrared band by Lipert and Muhle.* In the remanent state it has been previously reported that application of an alternating field produces an effect identical with that of a static field of comparable strength.

**DISCUSSION**

Note that the "collective" mode predicted theoretically \( n \) also a resonance of the single-dipole motion. For H\(_2\)CO, PCl, and CHCl\(_3\), liquids Lobo et al. estimate collective mode frequencies in the 300-600 cm\(^{-1}\) region. However,
Fig. 2.—Decrease and subsequent increase of integrated absorption intensity of salinex with application of an external electric field.

Fig. 1.—Plot of log A/log I against z for liquid salinex. Here I is the absorption intensity in the absence of an electric field and I is with an electric field applied. (1) 3.0, (2) 2.3, (3) 5.0, (4) 7.0 kV cm⁻¹.

Our results do not substantiate the prediction of collective modes at 0.5-5.0 cm⁻¹ for a number of simple benzene derivatives. If this is due to quantitative deficiencies in the Nee-Zwanzig evaluation then the use of structural and electrical characteristics rather than field equations might improve the agreement between theory and experiment.

Lippert and Michel observed their effects in liquid acetonitrile, using static electric fields of up to 5 x 10⁵ V cm⁻¹. With increase in the electric field a rapid decrease of intensity can be observed in the 2250 cm⁻¹ band, while the other mid and near infrared bands show effects similar to that of heating. A similar phenomenon can be observed in the far infrared for salinex (fig. 3) where the integrated intensity rapidly falls with the application of the field and then rapidly regains its original level when the field is switched off. In acetonitrile the field effect was interpreted in terms of excitations of the π-electrons. Indeed Lippert and Michel have suggested the existence of a "pre-solid" state of matter on this and related evidence,
such as the sudden increase in the maximum intensities of the normal modes coupled with a sudden decrease in the coordination modes. The state is due to cooperative dynamic phenomena originating from a coupling of molecular oscillations. The cooperative oscillation reduces the distance between the molecules, destroys individual rotational freedom and leads to the characteristic interactions and dynamics of the solid state. To support this conjecture in liquid acetone these authors cite as evidence the local asymmetry in the structure of liquid acetone, revealed by X-ray analysis. There is an asymmetry in the perpendicular intermolecular distances despite the fact that the perpendicular potentials are symmetric.

At this stage it is relevant to discuss the role of the wave vector \( k \) in a zero-THz spectrum. If for some reason this remains finite in such an experiment then the spectrum would be capable of yielding information on density fluctuations, or large scale collective motions propagated electrodynamically. If we deal with a Kirkwood correlation sphere containing a large number of molecules the relevant zero-THz correlation function is in fact:

\[
\frac{1}{k} \sum_{j} k \cdot p_{j} \exp[i k \cdot r_{j}(0)] \sum_{j} k \cdot p_{j} \exp[-i k \cdot r_{j}(0)]
\]

where the sum runs over all molecules within the Kirkwood sphere, centred on \( r_{j}(0) \), the position vector of the centre of mass of molecule \( j \). The \( k \cdot n \) signifies that it is the polarisation charge density which responds to a scalar probe, not the polarisation, as is usually tacitly assumed. Reduction to the classical Kirkwood theory is possible only for \( k \rightarrow 0 \), the hydrodynamic limit,

\[
\frac{1}{k^2} \sum_{j} p_{j}(0) \cdot \sum_{j} p_{j}(0)
\]

In a fluid made up of ions, of course, we may define a charge density via the Poisson equation:

\[
V = \frac{e_{0} q_{p}}{2}
\]

where \( q \) is the particle charge and \( e_{0} \) is an external applied electric field. If we then use hydrodynamic equations to describe the liquid a term proportional to \( k \cdot r \) must be added to the Navier-Stokes equation. When solved this leads directly to a plasma frequency \( \omega_{p} = \sqrt{e_{0} q_{p}^{2}/m} \), where \( m \) is the particle mass. The frequency of collective oscillations does not vanish as \( k \rightarrow 0 \) in this case, but \( \omega_{c} \). This collective oscillation in the ionic fluid is called the plasmon and may be simulated by computer molecular dynamics. If we substitute for the charge density the polarisation charge density then it is clear that zero-THz spectroscopy with finite \( k \) leads to information on "plasmons" in dipolar but molecular (as opposed to ionic) fluids.

As \( k \rightarrow 0 \) in an ionic fluid, the density fluctuations are dominated by the plasma oscillations. In some cases (e.g., molten salts) it is possible to separate and identify the fluctuations in density and charge in density. The former determine sound wave propagation and the latter the plasmons, or plasma oscillations. These are liquid-state analogues of the acoustic and optic longitudinal phonons in an ionic crystal. These show up in the far infrared for both ionic and molecular crystals. Obviously the plasmon frequency of polarisation charge density fluctuations in a molecular fluid is the liquid-state analogue of the longitudinal optical phonon mode in the far infrared of the molecular crystal. All these propagative modes depend on the mutual interaction of molecular rotation and translation, the molecular crystal phonon modes being of course classifiable into those of translational and those of rotational origin.
The spectra therefore corroborate the evidence put forward by Ascarelli and Lobo et al. for internal field propagated intensity changes (fig. 1 in liquids where dipole-dipole interaction is strong). The formalism of Lobo et al. is identical with that extensively used by Evans et al., provided the latter’s equations are modified using the dynamic internal field, or dielectric friction concept of Nee and Zwanzig.

The effect of including the internal field theoretically is to decrease the integrated absorption intensity when expressed in terms of $\alpha(\omega)$, the power absorption coefficient, and to shift the peak in $\varepsilon'(\omega)$ to lower frequencies (fig. 1). The correction of Lobo et al. introduces no significant new feature into the three variable theory of Evans et al. or of Madden and Kivelson. This is to say that the poles $\varepsilon''(\omega) \rightarrow 0$ and $\varepsilon''(\omega) \rightarrow \infty$ labelled by these authors as plasmons are not specifically electrodynamic in origin but are rather natural spectral consequences of the particular Mori approximant used.

The S.R.C. is thanked for financial support.


(PAPER 9/1519)